

Observations Of A Cast Cu-Cr-Zr Alloy

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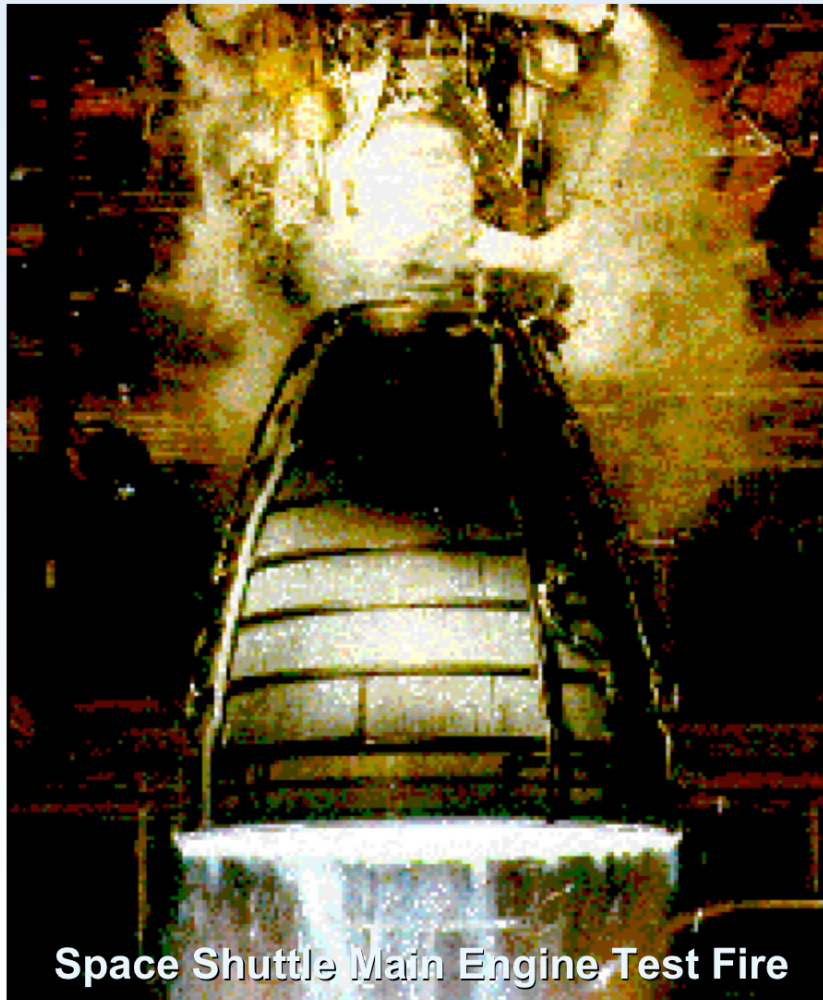
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Copper Alloys For Rocket Engine Main Combustion Chamber Liners



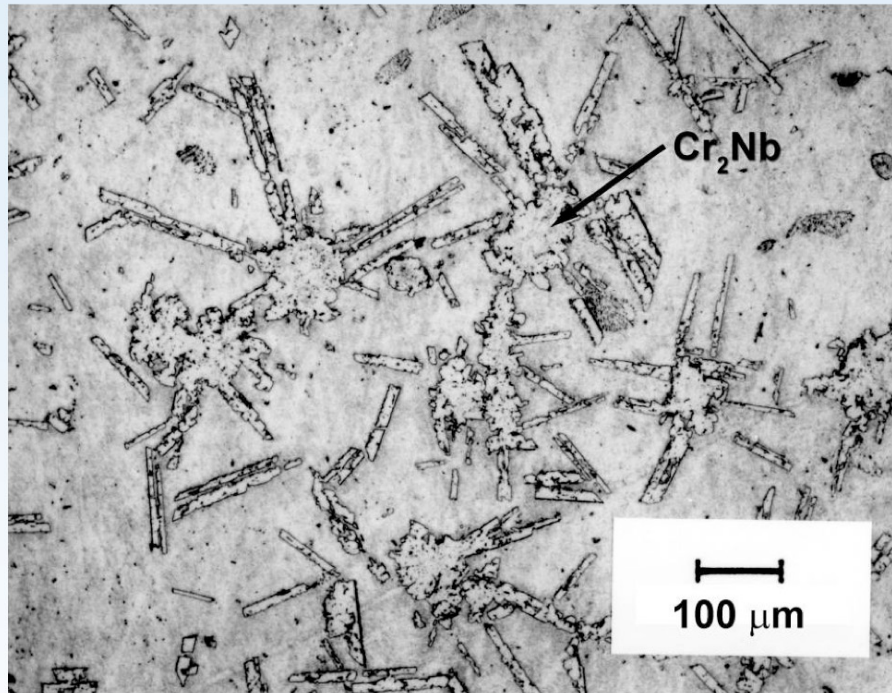
Space Shuttle Main Engine Test Fire

- **Requirements**
 - High Thermal Conductivity
 - Low Cycle Fatigue Resistance
 - Creep Resistance
 - Maximum Operating Temperature Above 500°C (932°F)
 - Good Elevated Temperature Tensile And Compressive Strengths
- **Current And Potential Alloys**
 - GRCop-84 (Cu-Cr-Nb)
 - NARloy-Z (Cu-Ag-Zr)
 - AMZIRC (Cu-Zr)
 - Glidcop AL-15 (Cu-Al₂O₃)
 - Cu-Cr
 - Cu-Cr-Zr

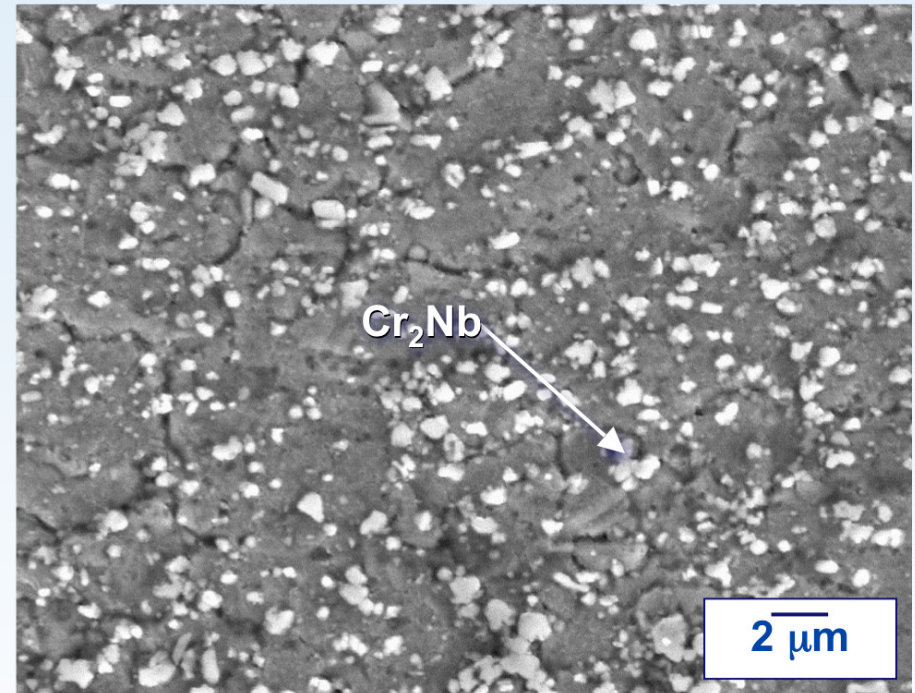
GRCop-84

- **First new liner material in nearly 40 years**
 - Primarily a replacement for NARloy-Z (Cu-3 Ag-0.15 Zr) used in SSME engine liners
- **Composition is Cu-6.65 wt.% Cr-5.85 wt.% Nb (Cu-8 at.% Cr-4 at.% Nb)**
- **GRCop-84 developed as a precipitation / dispersion strengthened alloy with good mechanical properties up to 700°C (1292°F)**
- **Strengthened by fine Cr₂Nb particles**
 - Cr and Nb have minimal solid solubility, high liquid solubility
 - Cr and Nb form high melting point (1733°C/3151°F), very hard (2000 KHN) compound

Typical GRCop-84 Microstructures



Typical Cast Microstructure

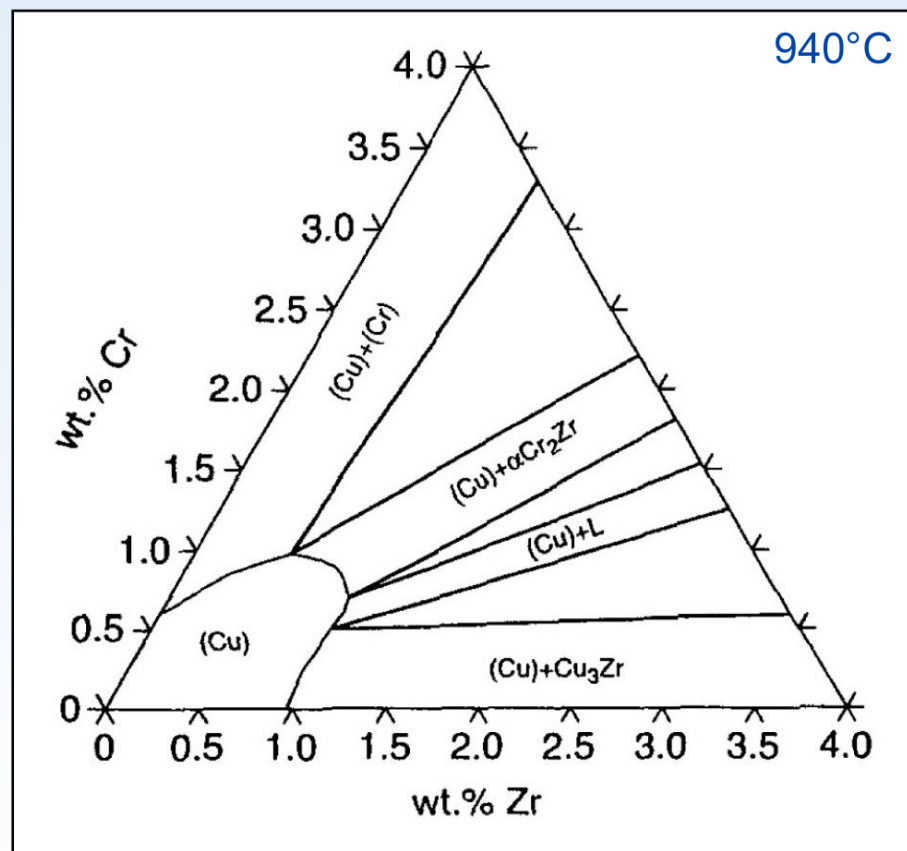


**Typical Consolidated
P/M Microstructure**

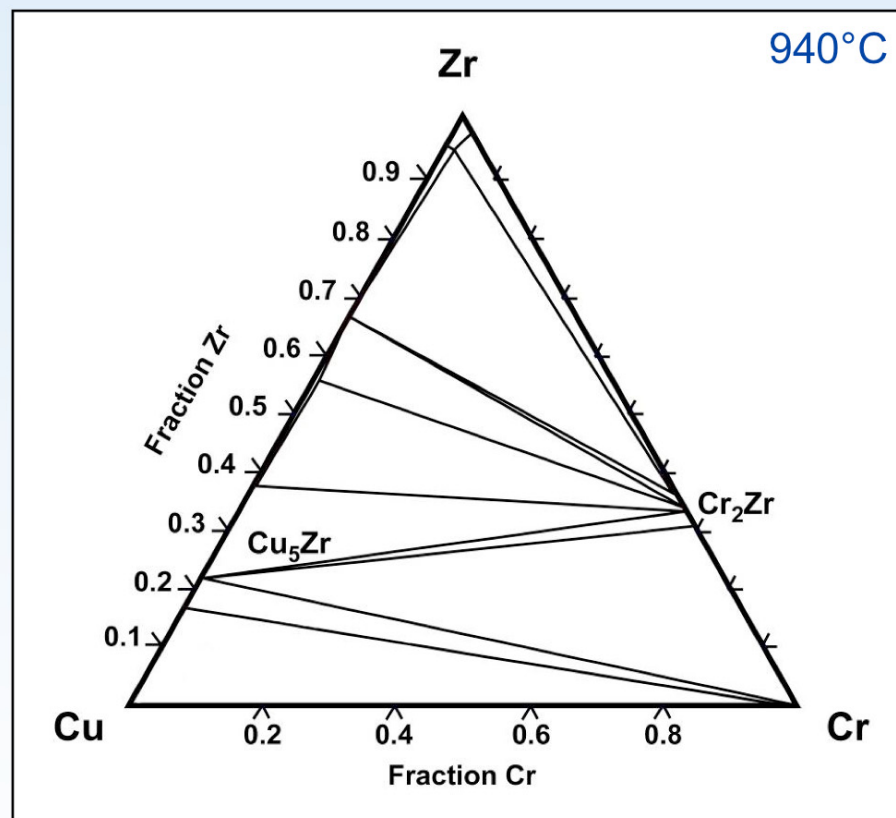
Rationale For Replacing Nb With Zr

- **Nb (element 41) and Zr (element 40) have many similarities in their chemical and physical properties**
- **Nb and Zr both form very similar intermetallic compounds with Cr**
 - Cr_2Nb and Cr_2Zr both have C_{15} cubic structure and an $\text{Fd}3\text{m}$ or Cu_2Mg space group
 - Lattice parameters are nearly identical
 - Cr_2Nb – 0.699 nm
 - Cr_2Zr - 0.721 nm (+3%)
- **Cr_2Zr has a lower melting point (1380°C versus 1733°C) so melt temperatures in powder production can be lowered**
- **Zr appears to have a strong beneficial effect on the Low Cycle Fatigue lives of copper-based alloys**
 - LCF is generally the most important mechanical property for rocket engines
- **Coarse cast microstructures with desired phases could be refined through powder atomization**

Cu-Cr-Zr Ternary Phase Diagrams



Zahkarov et al (1957)

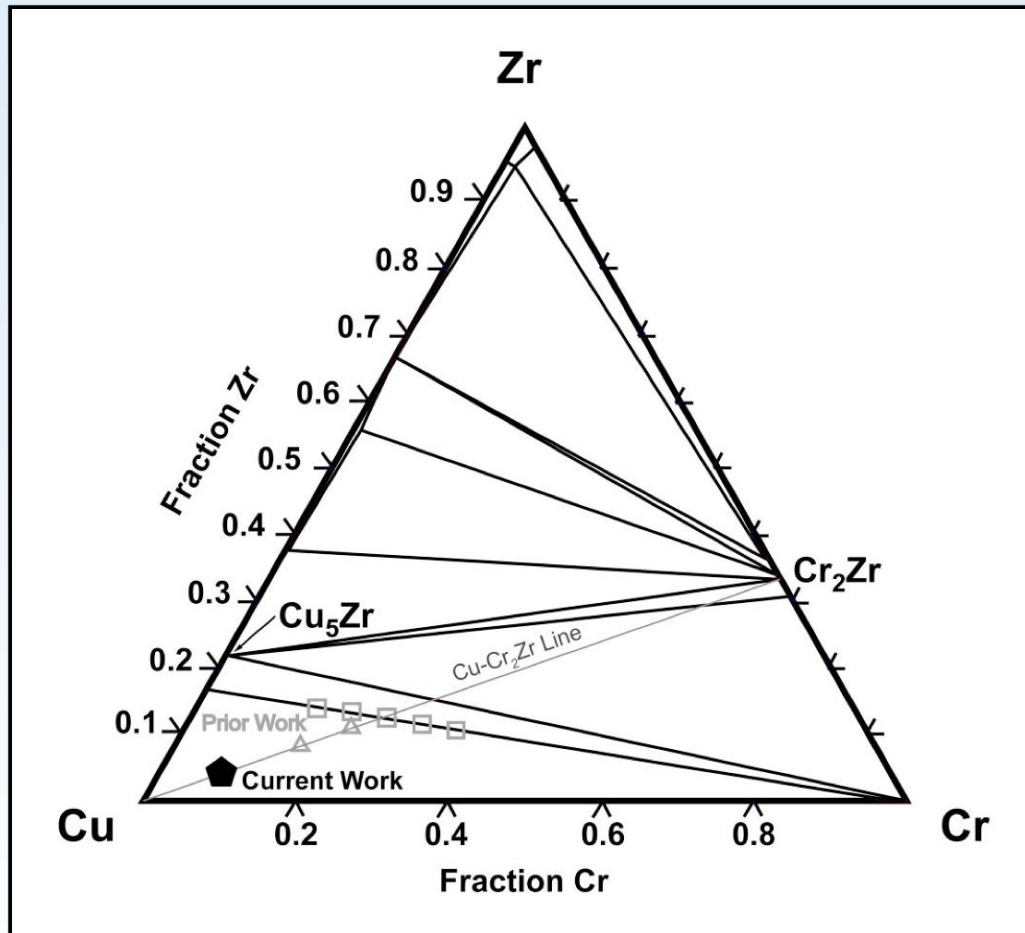


Zeng et al (1995)

Goals Of Research

- Determine if Zr can be directly substituted for Nb in GRCop-84 to form Cu-Cr₂Zr microstructure
- If the as-cast microstructure did not have the desired phases, determine if Cr₂Zr could be formed by high temperature exposure and/or aging heat treatments

Current And Past Work



Compositions of Alloys From Zeng et al and Current Work

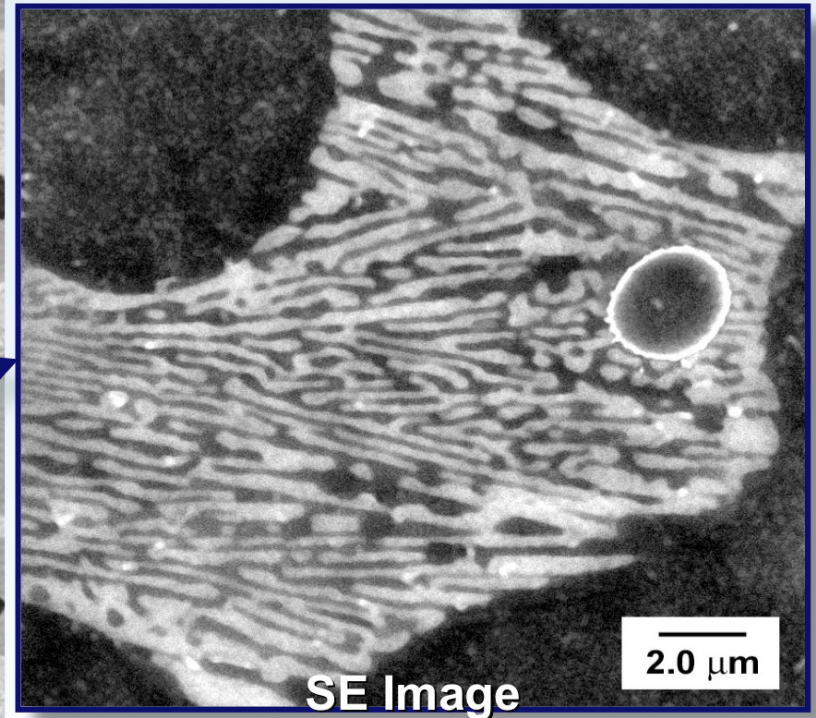
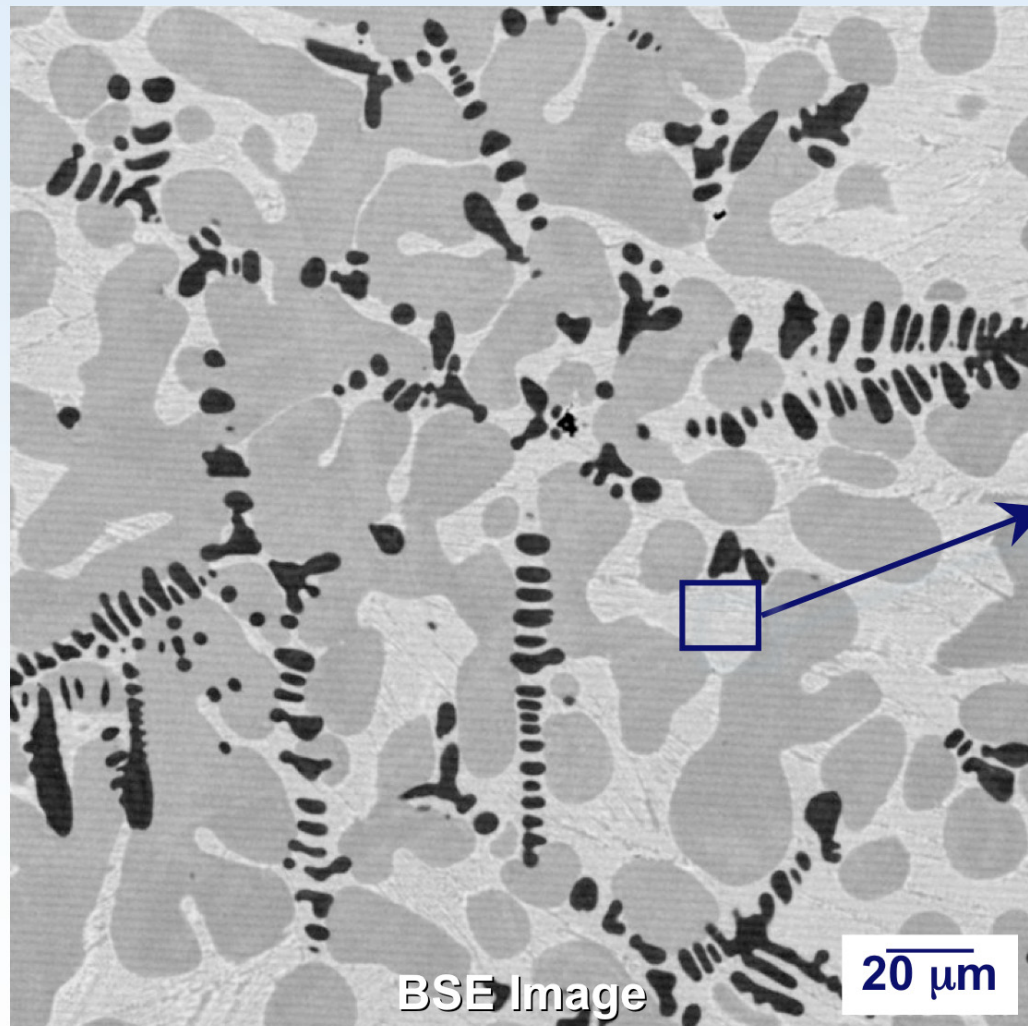
Alloy	Cu	Cr	Zr
CUZR-1	70.0	16.0	14.0
CUZR-2	65.8	21.0	13.2
CUZR-3	61.7	26.0	12.3
CU ZR-4	57.5	31.0	11.5
CUZR-5	53.3	36.0	10.7
CRZR-1	75.0	16.7	8.3
CRZR-2	67.0	22.0	11.0
Current Study	88.9	7.5	3.6

K. J. Zeng and M. Härmäläinen, *Journal of Alloys and Compounds*, Volume 220, Issues 1-2, (1 April 1995), pp. 53-61.

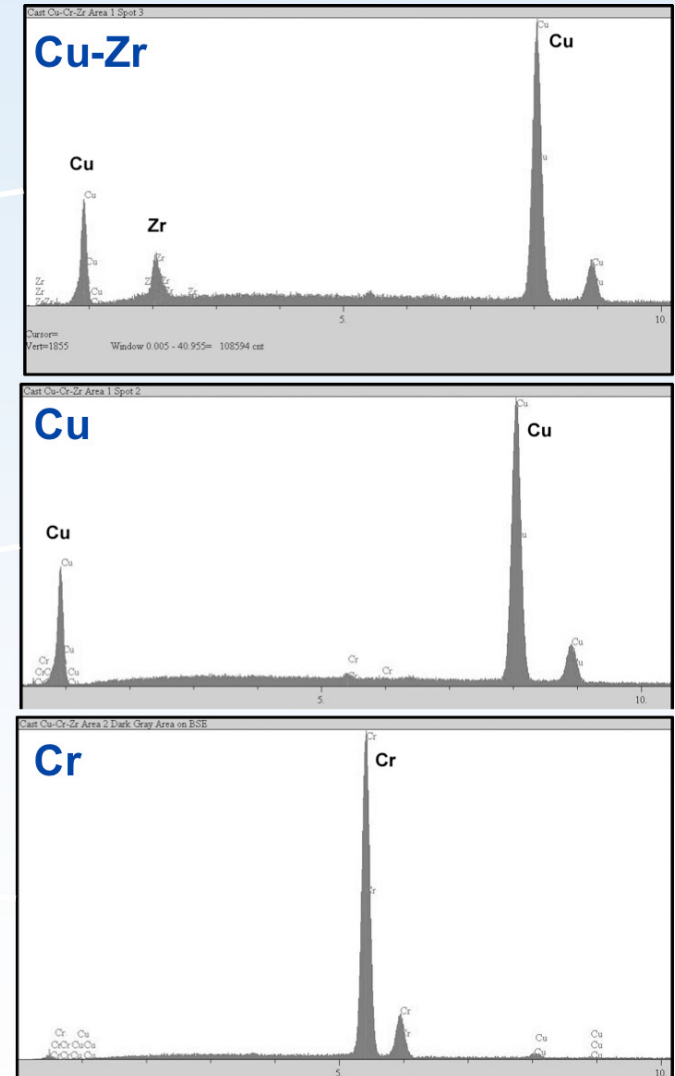
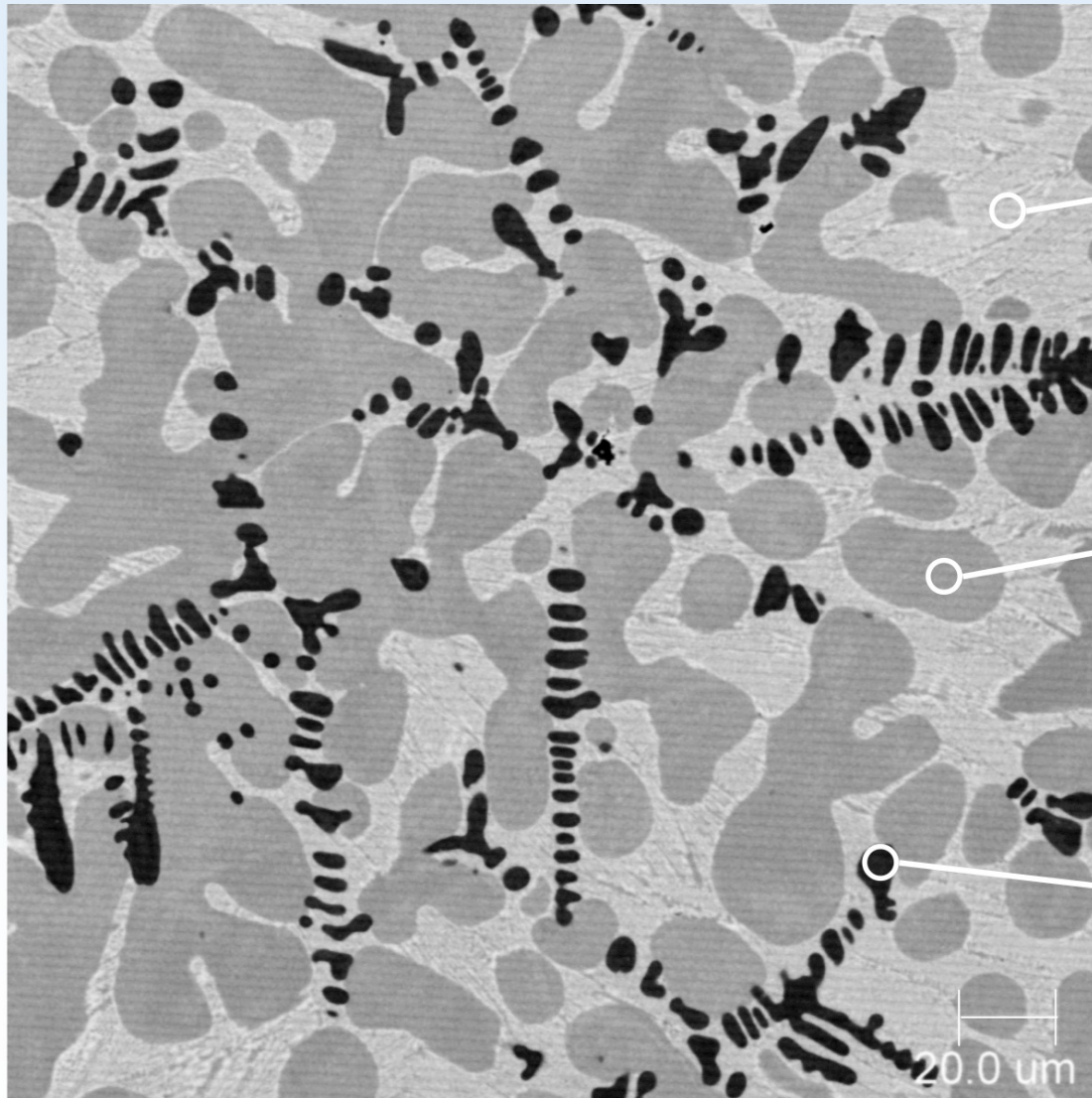
Cast Alloy Composition

Element	Weight Percentage	Atomic Percentage
Cu	Bal.	Bal.
Cr	6.15	7.54
Zr	5.25	3.60
Fe	30 ppm	-
N	6 ppm	-
O	159 ppm	-
S	10 ppm	-
Y	150 ppm	-

Typical As-Cast Microstructure



Energy Dispersive Spectroscopy (EDS)



Quantitative Microprobe Analysis

Microstructural Feature	Cu (wt.% / at. %)	Cr (wt.% / at. %)	Zr (wt.% / at. %)	Phase(s)
Overall Lamellae	88.4 / 90.6	0.5 / 0.6	12.0 / 8.6	Cu + Cu ₅ Zr
Light Lamella	76.9 / 82.1	0.7 / 1.0	22.7 / 16.9	Cu ₅ Zr
Dark Lamella	99.1 / 99.0	0.6 / 0.8	0.3 / 0.2	Cu
Cr dendrites	2.4 / 2.0	97.4 / 98.0	0.0 / 0.0	Cr
Cu dendrites	99.3 / 99.4	0.1 / 0.1	0.4 / 0.6	Cu

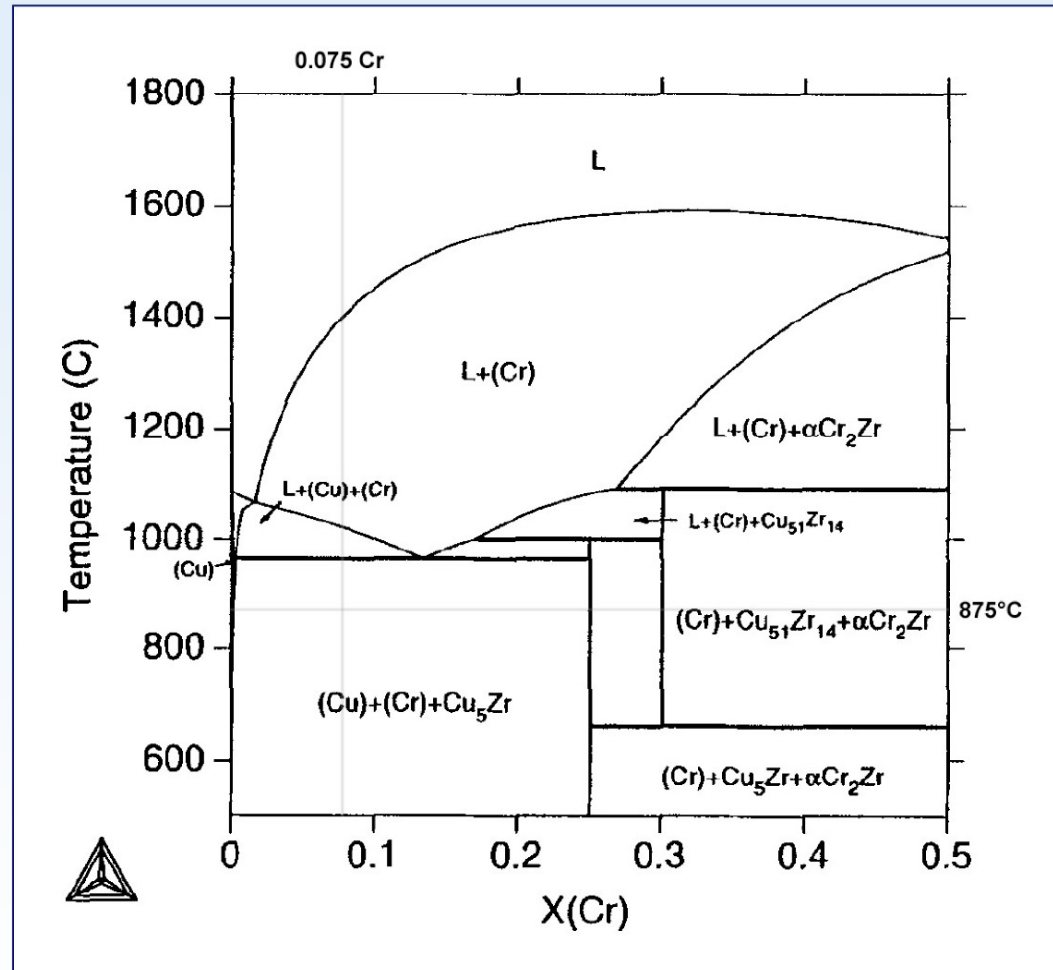
- **JEOL 8200 Superprobe with five WDS and one EDS detectors allowed for simultaneous measurement of all three major elements of interest**
- **Results are consistent with Zeng et al**

Volume Fraction Of Each Phase

Phase	Volume Fraction
Cr	10.1%
Cu	62.0%
Cu ₅ Zr	27.9%

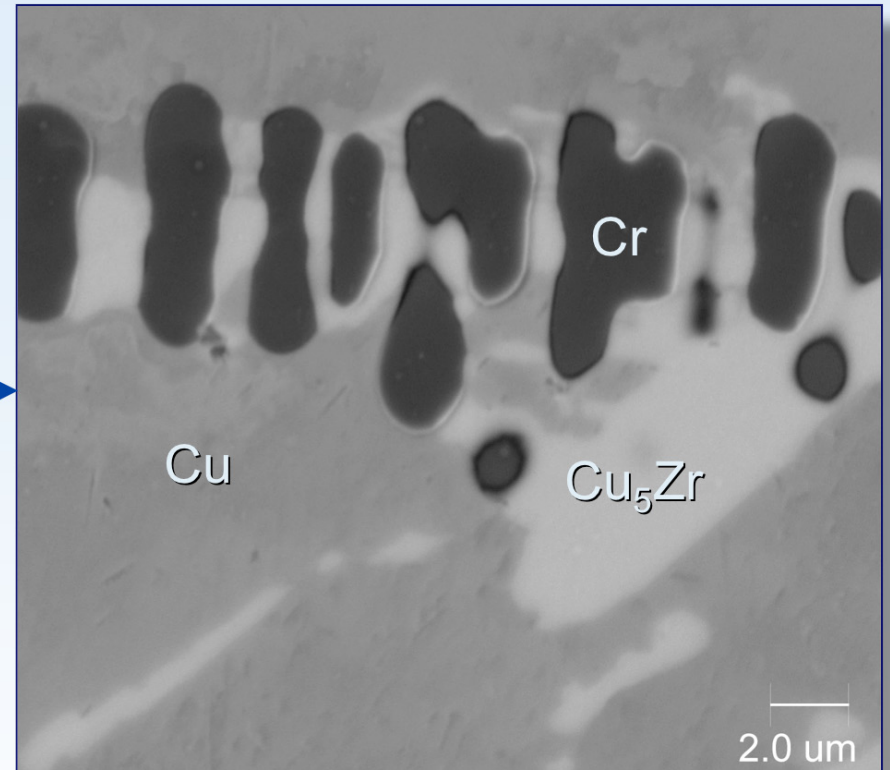
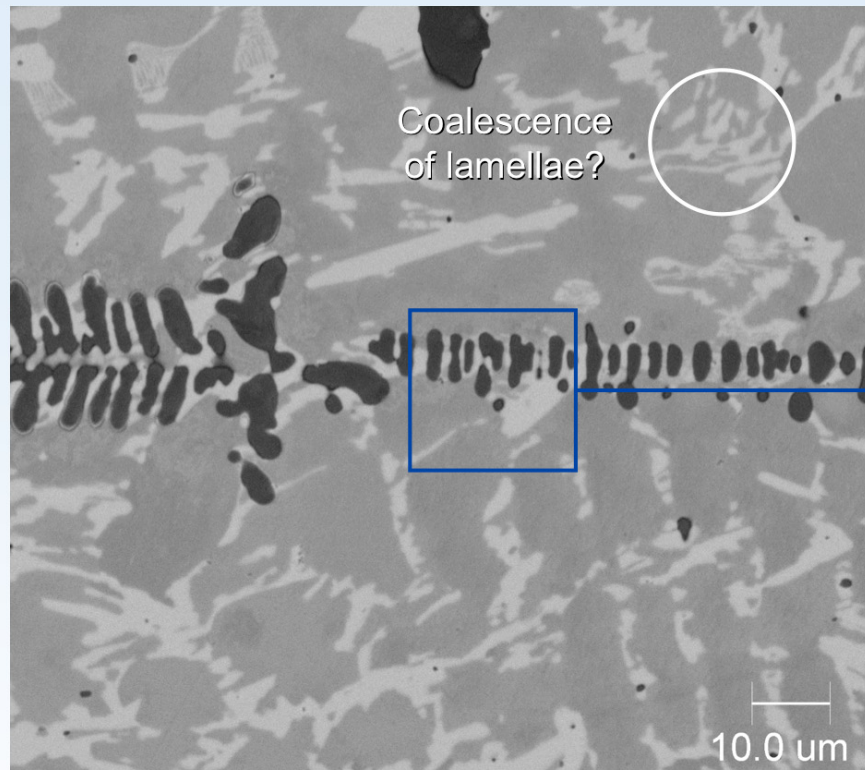
- Volume fractions determined from average of five images using automated image analysis
- Slight inconsistencies with volume fractions from ternary phase diagram attributable to experimental error in measurement techniques

Cu-Cr₂Zr Vertical Section



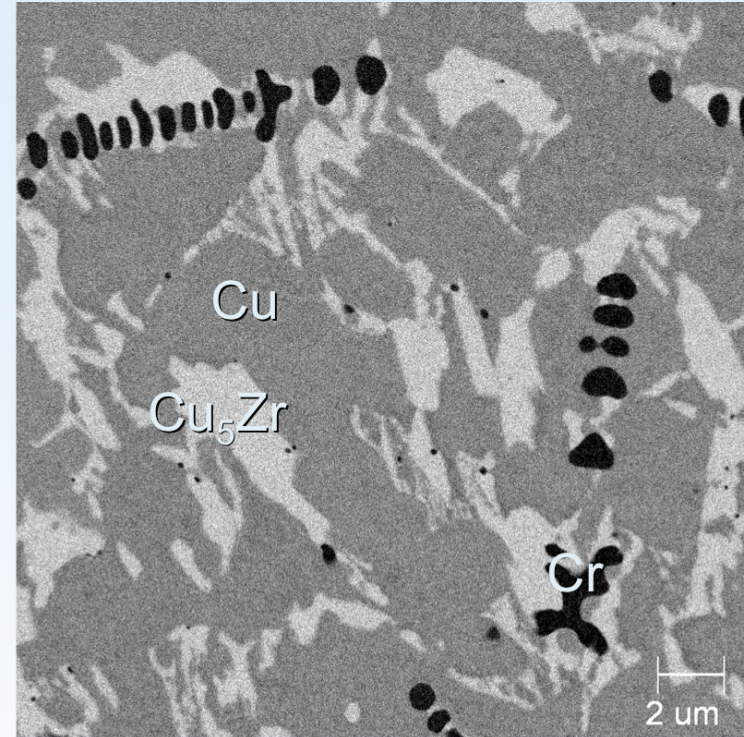
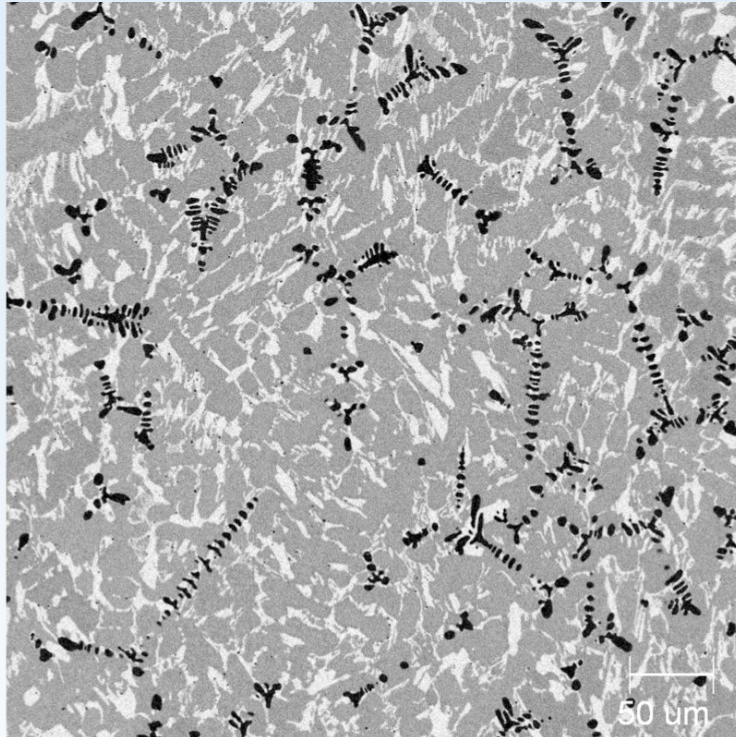
Vertical section from Zeng et al's Cu-Cr-Zr phase diagram indicates that the three observed phases are only ones expected

Effect Of High Temperature Heat Treatment



- **Exposed at 875°C (1607°F) for 176.5 h**
 - Temperature selected based on Cu-Zr phase diagram to avoid incipient melting
- **Lamellae could no longer be resolved at 10,000X but Cu₅Zr peaks observed in X-ray diffraction**
- **No Cr₂Zr detected at Cr-Cu₅Zr interface**
- **Microstructural evidence suggests that lamellae either coalesced or coarsened during heat treatment**

Effect Of Aging



- **Aged at 425°C (797°F) for 4 hours**
 - Temperature same as aging temperature for AMZIRC (Cu-0.15 Zr)
- **No detectable changes in microstructure**
- **Additional peaks observed in X-ray diffraction**
 - Definite peaks – Cu, Cr, Cu₅Zr
 - Possible peaks – Zr, metastable phase(s)?

Summary and Conclusions

- **The calculated phase diagram and observations of Zeng et al were confirmed**
 - Additional X-ray diffraction peaks for aged sample indicates possibility that additional metastable phases may form
 - Cu_5Zr was observed rather than the Cu_9Zr_2 proposed for the binary Cu-Zr phase diagram
- **Despite similarities between Zr and Nb, Cu-Cr-Zr does not appear to be a good candidate alloy system for rocket engine applications**